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CONSTITUENT MATERIAL OF FUSED CARBONATE TYPE FUEL CELL

X 1-3, 6, 8-11

all alloys have Cr (claim 5)
Al_2O_3 ??
no carbon - claim 4

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Applicant(s)::	AGENCY OF IND SCIENCE & TECHNOL; others: 01
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Equivalents:	JP2050434C, JP7066824B

Abstract

PURPOSE:To improve the strength and corrosion resistance by specifying a composition of Cr, Al, Co and/or Ni and the residual of Fe and unavoidable impurities.
CONSTITUTION:As the constituent material, Cr: 0.5-30% (weight%; the same hereinafter), Al: 0.5-10%, Co and/or Ni: 0.5-7% and the residual of Fe and unavoidable impurities are used. Cr and Al form corrosion-resistant lithium chromate lithium aluminate coatings, respectively, under a fused carbonate environment comprising Li_2CO_3 and K_2CO_3. Also, Co and/or Ni play a role of good adhesion between these coatings and the material, resulting in an improved strength and corrosion resistance.

ISK doc

AGEN ★ X16 88-319147/45 ★J63236-267-A

Material for fused carbonate fuel cell - comprises chromium, aluminium, cobalt and/or nickel and iron and opt. silicon

AGENCY OF IND SCI TECH (KOBM) 20.03.87-JP-067623

L03 M27 (03.10.88) C22c-38 H01m-04/86 H01m-08/02

20.03.87 as 067623 (93MD)

The constitutional material comprises by wt.0.5-30% Cr, 0.5-10% Al, 0.5-7% Co and/or Ni, and balance Fe and impurities.

The material may contain 0.5-10% Si.

USE - The material has good strength, corrosion resistance, workability and is cheap. (4pp Dwg.No.0/0)

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※　審査請求　有　発明の数　2　（全4頁）

㊹発明の名称　溶融炭酸塩型燃料電池構成材料

㉑特　願　昭62－67623
㉒出　願　昭62(1987)3月20日

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最終頁に続く

明　細　書

1．発明の名称

溶融炭酸塩型燃料電池構成材料

2．特許請求の範囲

(1) Cr：0.5～30％（重量％、以下同じ意味）

Al：0.5～10％

Coおよび／またはNi：0.5～7％

残部Feおよび不可避不純物からなることを特徴とする溶融炭酸塩型燃料電池構成材料。

(2) 特許請求の範囲第1項において、

Cr：0.5～10％とした溶融炭酸塩型燃料電池構成材料。

(3) Cr：0.5～30％

Al：0.5～10％

Coおよび／またはNi：0.5～7％

Si：0.5～10％

残部Feおよび不可避不純物からなることを特徴とする溶融炭酸塩型燃料電池構成材料。

(4) 特許請求の範囲第3項において、

Cr：0.5～10％とした溶融炭酸塩型燃料電池構成材料。

3．発明の詳細な説明

［産業上の利用分野］

本発明は強度および耐食性に優れ、かつ市場性、加工性、経済性に優れた溶融炭酸塩型燃料電池構成材料に関するものである。

［従来の技術］

溶融炭酸塩型燃料電池は、エネルギー変換効率が高く、公害発生がなく、かつ高価な触媒を必要としない等の利点があることから、次世代の電源として有望視されており、現在は小規模な電池を組んで耐久性の検討を行うと共に積層技術の開発や、大規模化のための検討および電池の電極材料やその他の構成材料の開発が進められている。

［発明が解決しようとする問題点］

現状での問題として、溶融炭酸塩型燃料電池の電極やセパレーターなどの電池構成材料は一般に腐食を受け易く長期の耐久性を有しないという問題やニッケルカソード電極が溶解し、アノード近

傍で析出して電池寿命を短くするという問題がある。

これらの問題を解決するための種々の検討（たとえば、アルミナ酸化被膜形成による防食：特開昭58－217677、フェロアロイ電極：特開昭58－155662、電解質保持体に関するもの：特開昭56－82583、特開昭58－117656、リチウム添加金属酸化物粉末電極：特開昭58－165253、リチウムコバルトオキサイド微粒子焼結体を電極とする燃料電池：特開昭60－117566、高耐食性金属材料と複合酸化物より成る集電体：特開昭59－230263、電気化学的に活性な金属で被覆したセラミック粒子からなる電極材料：特開昭57－92753）が行われているが、いずれも市場性、加工性および経済性の観点から好ましくない。

上記した問題点に鑑み、本発明においては強度および耐食性に優れ、かつ市場性，加工性および経済性の良好な溶融炭酸塩型燃料電池構成材料を提供することを目的としている。

［問題点を解決する為の手段］

上記問題点を解決することのできた本発明の溶融炭酸塩型燃料電池構成材料とは

Cr：0.5 ～30％（重量％、以下同じ意味）

Al：0.5 ～10％

Coおよび／またはNi：0.5 ～7％

残部Feおよび不可避不純物からなることを構成要旨とし、必要によりこれらにSiを含有させることにより溶融炭酸塩環境下とくにその気相および気液界面部での耐食性を向上させることができ、またCrを0.5 ～10％に限定すると特にσ脆性に優れたものとなる。

［作用］

本発明者らは溶融炭酸塩型燃料電池構成材料について種々検討した結果、強度に優れ、かつ市場性、加工性及び経済性の良好な鉄系材料を基材とし、耐食性に優れた酸化物被膜を形成させるために必要な後述の合金元素を見い出し本発明を完成した。即ちCr，AlはLi$_2$CO$_3$およびK$_2$CO$_3$よりなる溶融炭酸塩環境下で耐食性に優れたリチウムクロメート被膜及びリチウムアルミネート被膜をそれぞれ形成する。またCoおよび／またはNiはこれらの被膜と素材間の密着性を強固にする働きを有する。また、特にSiは粒界を安定化させ気液界面部での耐食性を向上させCrの添加量を限定するとσ脆性の改善を可能とする。この溶融炭酸塩型燃料電池構成材料は使用中に若干のLi及びKがドーピングされるが、その後は長時間腐食環境に曝されても変質せず、鉄系材料を防食する効果を持つ。

次に各合金元素の添加限定量および限定理由について述べる。

Cr：

Crは溶融炭酸塩浴中で安定なリチウムクロメート被膜を形成する元素であり、その効果を有効に発揮させるには0.5 ％以上の含有量が必要である。ただCr単独ではフェロクロム程度のCrが含有されていないと素材の防食効果を十分に発揮する程度のリチウムクロメートが生成されず、Al，Ni，Coなど他の金属元素あるいは酸化物と共存することによって、低Cr含有量でも耐食性の良好な被膜を形成する。また特にσ脆性を考慮すると0.5 ～10％が良い。

Al：

Alは溶融炭酸塩浴中で単独で安定なリチウムアルミネート被膜を形成し、電極材料の耐食性を著しく向上させる。0.5 ％未満では耐食性改善効果が小さく、10％を超えると被膜の密着性が低下し、耐食性が低下する。

Co：

Coは鉄系素材と被膜、すなわちリチウムクロメート被膜やリチウムアルミネート被膜の密着性改善に有効な元素であり、鉄系材料の表面に生成するスピネル酸化物をアモルファス化することにより密着性を改善する効果がある。但し0.5 ％未満では顕著な効果が認められない。一方Co含有量が多過ぎると溶出したCoがアノード近傍に析出して電池性能低下の原因となるので7％を上限

とした。

Ｎｉ：

Ｎｉは Ｃｏと同様の効果があり、またＣｒ酸化物やＡｌ酸化物中に共存すると、被膜の防食性能を向上させる効果がある。0.5％未満では顕著な効果が認められず、Ｎｉ含有量が多過ると溶出したＮｉがアノード近傍に析出して電池性能低下の原因となるので７％以下とした。

Ｓｉ：

Ｓｉは溶融炭酸塩環境化特に気液界面部での材料表層部の結晶粒界を安定化させ耐食性向上に効果がある。しかし0.5％ではその効果が著しく低下し、一方１０％を超えるとSiO_2が大量に生成して耐食性を低下させる。

［実施例］

第１表に示す組成の合金を６５０℃、６２mol％Li_2CO_3＋３８mol％K_2CO_3浴中に浸漬し１カ月後の腐食率およびσ相析出の有無を調べた結果を第１表に示す（成分係数は重量％を意味し残りはＦｅおよび不可避不純物である）。

第　１　表

	No.	成　　分	腐食率[*1]	σ相析出の有無
本発明例	1	9Al－4Cr－2Ni－7Si	0.013	無
	2	5Al－7Cr－0.5 Co	0.013	無
	3	1Al－17Cr－1Ni－1Si	0.034	無
	4	1Al－13Cr－1Co－1Si	0.030	無
	5	5Al－9Cr－4Ni－1Si	0.012	無
	6	5Al－10Cr－2Ni	0.007	無
	7	5Al－20Cr－2Co	0.003	有
比較例	8	100％Ni	1.086	無
	9	18Cr－11Ni－1Si	0.120	有
	10	8Al－92Ni	0.053	無
	11	5Al－20Cr	0.580	有
	12	13Al－5Si	0.783	無
	13	4Al－8Si	7.764	無
	14	10Si－90Ni	5.934	無
	15	5Al－7Si－88Ni	2.912	無

*1：単位　$g/m^2\,hr$

［650℃、62mol％Li_2CO_3＋38mol％K_2CO_3浴の界面部、１カ月試験
ガス雰囲気．CO_2：O_2＝2：1］

No.１～７は本発明で限定した成分組成の合金、No.８～１５は比較例である。

No.１～７は腐食率が優れており、Ｃｒ１０％以下のものは本発明例．比較例ともにσ脆性にすぐれている。

（以下余白）

［発明の効果］

以上のように本発明の溶融炭酸塩型燃料電池構成材料は強度および耐食性に優れ、かつ市場性、加工性、経済性に優れたものである。

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第1頁の続き

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54 Title of Invention: Structural Material for Fused Carbonate Type Fuel Cell

21 Patent Application Number: 62-67623

22 Date of Application: 20th March 1987

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SPECIFICATIONS

1. Title of the Invention

Structural Material for Fused Carbonate Type Fuel Cell

2. Claims

1. A structural material for a fused carbonate type fuel cell, such material characterized by consisting of

   Cr: 0.5% to 30% (wt%; similarly below)

   Al: 0.5% to 10%

   Co and/or Ni: 0.5% to 7%

   with the balance being Fe and the inevitable impurities
2. A structural material for a fused carbonate type fuel cell as in Claim 1, such material characterized by consisting of 0.5% to 10% Cr
3. A structural material for a fused carbonate type fuel cell, such material characterized by consisting of

   102 1, 2, 3,

   Cr: 0.5% to 30%

   Al: 0.5% to 10%

   Co and/or Ni: 0.5% to 7%

   Si: 0.5% to 10%

   with the balance being Fe and the inevitable impurities
4. A structural material for a fused carbonate type fuel cell as in Claim 3, such material characterized by consisting of 0.5% to 10% Cr

3. Detailed Description of the Invention

Relevant field of industry

This invention relates to a structural material for fused carbonate type fuel cells, such material having excellent resistance to corrosion, and being highly marketable, workable and economical.

Prior art

Fused carbonate fuel cells possess the advantages of having high energy conversion rates, not causing pollution, and not requiring expensive catalysts and so forth, and hence are highly regarded as next generation electricity sources, and at present, research and active technical development are proceeding on the durability of small-sized cells, while research is proceeding into increasing the size of such cells and into the development of the electrode materials and other structural materials in such cells.

Problems addressed by the present invention

At present, the problems of fused carbonate type fuel cells are that the fuel cell structural materials such as the electrodes and separators and so forth are generally readily corroded and do not possess long-term durability, and that the nickel cathodes dissolve and precipitate in the vicinity of the anodes, thus reducing the service life of the fuel cells.

Various research projects have been conducted in order to overcome these problems (for example, prevention of corrosion by forming alumina-oxide film – JP58-217677; ferroalloy electrodes – JP58-155662; electrolyte holders – JP56-82583 and JP58-117656; lithium-doped metal oxide powder electrodes – JP58-165253; fuel cells with electrodes formed of lithium-cobalt oxide particle sinter – JP60-117566; current collectors consisting of highly corrosion-resistant metal materials and composite oxides – JP59-230263, and electrode materials consisting of ceramic particles coated with electrochemically active metals – JP57-92753) but none of these have been preferable from the viewpoints of marketability, workability and economics.

essentially teaches away from Al_2O_3?

The present invention takes account of these problems, and it is an objective of the present invention to provide a structural material for fused carbonate type fuel cells, such material being highly resistant to corrosion, and being very marketable, workable and economical.

Means employed in order to overcome these problems

In order to overcome these problems, the structural material for fused carbonate type fuel cells envisaged by the present invention consists essentially of

Cr: 0.5% to 30% (wt%; similarly below)

Al: 0.5% to 10%

Co and/or Ni: 0.5% to 7%

with the balance being Fe and the inevitable impurities, with Si being included where necessary whereby it is possible to improve resistance to corrosion in a fused carbonate environment, and particularly at the gas phase and the gas-liquid phase boundary, and in which σ embrittlement is excellent because Cr is restricted to between 0.5% and 10%.

Action

As a result of extensive research into structural materials for fused carbonate type fuel cells, the inventors of the present invention discovered the alloy elements described above that are required for an iron-based substrate that has excellent strength and good marketability and workability, and for the formation of an oxide film that has excellent resistance to corrosion, and so perfected the present invention. Thus, Cr and Al form respectively lithium chromate films and lithium aluminate films that have excellent resistance to corrosion in fused carbonate environments that consist of Li_2CO_3 and K_2CO_3. Moreover, Co and/or Ni act to strengthen the adhesion between such films and the substrates. Moreover, Si stabilizes the grain boundaries and enhances the resistance to corrosion at the gas-liquid phase boundary, and σ embrittlement can be improved by restricting the amount of Cr that is added. Such structural materials for fused carbonate type fuel cells are doped with small amounts of Li and K in use, but thereafter undergo no change even when exposed for long periods of time to corrosive environments, and the iron materials are protected against corrosion.

Next, the limits on the amounts of each of the alloying elements added, and the reasons therefore, are described.

Cr:

Cr is an element that forms a stable film of lithium carbonate in a fused carbonate bath, and not less than 0.5% of this element is required in order to usefully produce this effect. However, if Cr is not present to the extent of its presence in ferrochrome, lithium chromate sufficient to produce an excellent corrosion resistance is not formed, and when Cr is present in company with such alloying elements as Al, Ni and Co and the like, films with good corrosion resistance are formed, even at low Cr contents. Moreover, between 0.5% and 10% of Cr is preferred for reasons of σ embrittlement.

Al:

Al by itself forms a stable lithium aluminate film in the fused carbonate bath, and greatly enhances the resistance of the electrode material to corrosion. The corrosion resistance effect is slight if less than 0.5% Al is present, while the adhesion of the film is impaired and corrosion resistance is reduced, if more than 10% Al is present.

Co:

Co is an effective element in enhancing the adhesion of the iron substrate and the films, that is, of the lithium chromate and lithium aluminate film, and produces the effect of enhancing adhesion by rendering amorphous the spinel-oxide film that is formed on the surface of the iron substrate. However, no significant effects are observed if less than 0.5% Co is present. On the other hand, if too much Co is present, molten Co is deposited near the anode, causing a decline in cell performance, such that an upper limit of 7% Co is imposed.

Ni:

Ni has similar effects to Co, and also has the effect of enhancing the resistance of films to corrosion when present in Cr oxides and Al oxides. However, no significant effects are observed if less than 0.5% Ni is present. On the other hand, if too much Ni is present, molten Ni is deposited near the anode, causing a decline in cell performance, such that an upper limit of 7% Ni is imposed.

Si:

Si stabilizes the grain boundaries at the surface of the materials at the gas-liquid boundary in a fused carbonate environment and has the effect of enhancing resistance to corrosion. However, at 0.5% Si content, the effect rapidly declines, whereas if more than 10% Si is present, large amounts of SiO_2 are formed and resistance to corrosion declines.

Practical embodiments

The alloys with the compositions shown in Table 1 were immersed in a bath consisting of 62 mol% Li_2CO_3 + 38 mol% K_2CO_3 at 650° C for one month, whereupon the alloys were examined for the rate of corrosion and for the presence of σ phase precipitation, with the results listed in Table 1 (composition factor is wt%, with the balance being Fe and the inevitable impurities). Numbers 1 to 7 are alloys whose composition was restricted to that of the present invention, and Numbers 8 to 15 are comparative examples.

Numbers 1 to 7 exhibited excellent resistance to corrosion, and both the practical embodiments of the invention and comparative examples with not more than 10% Cr exhibited excellent σ embrittlement.

Table 1

	No.	Composition	Corrosion rate*1	Presence of σ phase embrittlement
Present invention	1	9Al-4Cr-2Ni-7Si	0.013	No
	2	5Al-7Cr-0.5Co	0.013	No
	3	1Al-17Cr-1Ni-1Si	0.034	No
	4	1Al-13Cr-1Co—1Si	0.030	No
	5	5Al-9Cr-4Ni-1Si	0.012	No
	6	5Al-10Cr-2Ni	0.007	No
	7	5Al-20Cr-2Co	0.003	Yes
Comparative examples	8	100% Ni	1.086	No
	9	18Cr-11Ni-1Si	0.120	Yes
	10	8Al-92Ni	0.053	No
	11	5Al-20Cr	0.580	Yes
	12	13Al-5Si	0.783	No
	13	4Al-8Si	7.764	No
	14	10Si-90Ni	5.934	No
	15	5Al-7Si-88Ni	2.912	No

*1: Units g/m^2 hr (Boundary of 62 mol% Li_2CO_3 + 38 mol% K_2CO_3 bath, 650° C, tested for one month; environmental gas: $CO_2:O_2$ = 2:1)

Effects of the invention

The structural material for a fused carbonate type fuel cell envisaged by the present invention described above possesses excellent strength and resistance to corrosion, with excellent marketability, workability and economics.

Applicant: Director, Agency of Industry, Science and Technology

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